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THERMAL CONDUCTIVITY OF GRAPHENE INCORPORATED HEAT ACTIVATED POLYMETHYLMETHACRYATE: A PILOT STUDY

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Abstract:

Purpose: To evaluate whether the incorporation of graphene nanoparticles to PMMA improves its thermal conductivity properties. ***Materials and Methods:*** *In this in vitro experiment, samples of 10 PMMA acrylic disks, 5 disks with graphene nanoparticles (test group) and 5 disks without graphene nanoparticles (control group) were fabricated and subjected to thermal conductivity testing. The sample disks were placed between the two plates of the instrument. The results were analyzed using the Mann Whitney U- test ($p<0.05$).* ***Results:*** *PMMA disks without graphene additives showed superior thermal conductivity than the test group ($p= 0.028$).* ***Conclusion:*** *Under the given conditions, acrylic disks with graphene additives did not conduct heat more than the disks without graphene additives. Sographene did not significantly improve the thermal properties of PMMA.*

Key words: **graphene in dentistry, thermal conductivity, polymethyl methacrylate**

Various biomaterials are used in Prosthodontics to fabricate removable prostheses for completely and partially edentulous patients. One of the most commonly used materials with decades of evidence is polymethyl methacrylate (PMMA). Polymethyl methacrylate has stood the test of time as a denture base material and holds its efficacy as a satisfactory denture base material till date. It was introduced in the year 1937 by Dr. Walter Wright and has its pros and cons[1].

PMMA has been employed successfully as a denture base material owing to its light weight, ease of fabrication, low cost, acceptable aesthetics, biocompatibility, low water sorption, and adequate strength; at the same time, it has certain disadvantages such as low fatigue resistance, low coefficient of elasticity and low thermal conductivity. Among these, of prime concern is the low thermal conductivity of PMMA which reduces the gustatory response and palatability of food for the patient[2]. Improved thermal conductivity of polymethyl methacrylates would be a boon to removable denture wearers thereby resulting in enhanced the acceptance of these dentures.

"Thermal conductivity, of a substance, is defined as the quantity of heat in calories, or Joules, per second, passing through a body 1 cm thick with a cross section of 1 cm square when the temperature difference is 1-degree Celsius". The value of thermal conductivity for PMMA is 0.2 W/m/degree Celsius[3].

To overcome this shortcoming, various materials have been used to improve the thermal conductivity of PMMA. Metal oxides like aluminium oxide, titanium oxide, zirconium oxide, silicon carbide filler powders, hydroxyapatite ceramic powders, silver nanoparticles, and carbon particles have been incorporated and have improved the thermal conductivity without affecting the strength of the acrylic denture base. Also, metal denture bases have been used by many clinicians to overcome this disadvantage[1,4,5].

The present study was conducted to test if the addition of a material, named Graphene, improved the thermal properties of dental polymers or not. Graphene which is a basic construction of graphite consists of carbon atoms arranged in a honey-comb structure in the form of flat thick sheets. It has broad potential applications in biomedical engineering and biotechnology, such as in DNA detection, drug delivery, cancer therapy, etc. Owing to its various excellent mechanical, thermal, electrical and anti-microbial properties[6,7,8] graphene is now being used in dentistry for detection of bacteria in dental caries and periodontal disease, in restorative dentistry for strong dental fillings that do not corrode in the oral cavity, as fillers in dental adhesives to prevent secondary caries, in bone tissue engineering, in periodontal tissue regeneration, in cancer therapy, as coating on implants to improve osseointegration and lastly its antibacterial properties which kills bacterial cells through cell- wrapping and cell-trapping mechanism. Due to these enhanced capabilities, graphene is being incorporated in dental biomaterials such as metals, ceramics, and polymers. Different graphene derivatives can achieve good dispersion within different polymers and can be easily processed[8].

Previous studies have proved that the addition of graphene to PMMA does not affect the impact and flexural strength. They are also biocompatible and nontoxic in the oral cavity. Graphene has been proved to be a superior thermal conductor in other biomedical applications. But this valuable property has not been investigated in dentistry so far[6]. Swami P, Sanyal P, Guru R, Kore A[9] evaluated and

Fig.1: Materials used for the study

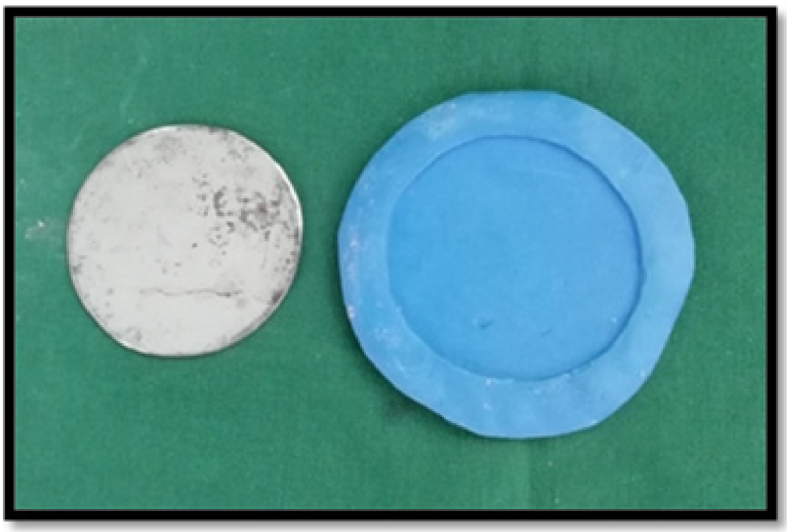


Fig.2: Steel molds

compared the addition of graphene and carbon fillers on the flexural and impact strength of PMMA. They concluded that 0.5% by weight of carbon fillers increased the flexural and impact strength of PMMA followed by graphene combined with 0.25% carbon and 0.25% graphene nanofillers.

Guazzo R[10] reviewed the uses of graphene nanomaterials in dentistry. They discussed the interaction between graphene nanomaterials with immune system cells and antibacterial activity of graphene nanomaterials. They concluded that further studies are required to evaluate the possible long term toxicity and their derivatives in the oral cavity. Malik S[11] described a new,easy and low-cost method to make large amount of FLG few layered graphene with multi-layered graphene and its inclusion into dental polymers. It was concluded that the new few layered graphene material incorporated in the dental polymer enhanced the physicomechanical properties as there was 27% increase in mean compressive strength and mean compressive modulus increased by 22%.

Shradhanjali A, Bouzid T, Sinitskii A, Lim J[12] and Kulshrestha S et al[7] reviewed the use of graphene for dental implant applications. Osseointegration of dental implants has been proven to improve after coating the implant surface with graphene oxide and reduced graphene oxide. The osteogenic differentiation of mesenchymal stem cells significantly improved on the implant surface and also increased the antibacterial properties. But further studies have to be done to reveal how graphene-based implant coatings would produce better implant actions. Lakshmi K, Rao GU, Arthiseethalakshmi S, Mohamed MSK[13] reviewed the properties, manufacturing methods, applications of graphene in general and biomedical fields and also in dentistry. In dentistry graphene is used for detection of bacteria in dental caries and periodontal disease, in restorative dentistry for strong dental fillings that do not corrode in the oral cavity, as fillers in dental adhesives to prevent secondary caries, in bone tissue engineering, in periodontal tissue regeneration, in cancer therapy, as coating on implants to improve osseointegration and antibacterial properties. Thus, they concluded that further research is needed for its use in dentistry.

The aim of this study is to investigate whether the addition of graphene nanoparticles in PMMA improves the thermal conductivity. Null hypothesis of this study is that the addition of graphene

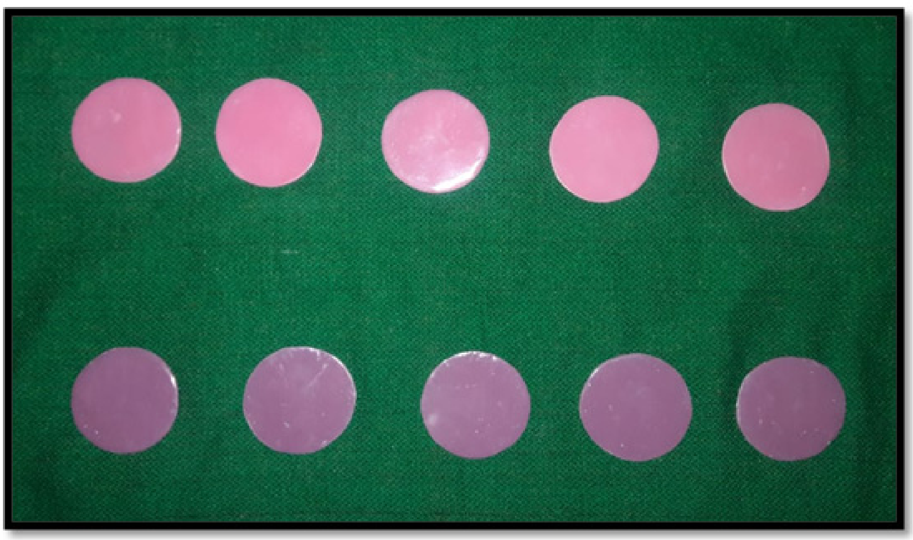


Fig.3: Control and test samples

Fig.4: Thermal conductivity tester

nanoparticles in PMMA does not affect the thermal conductivity.

Materials and methods

Two stainless steel disks were constructed by cutting solid stainless steel plates into the desired shape and dimension of 50 x 2±0.5mm (Fig.2)[14]. Ten putty molds, (Virtual, Putty Base Regular Set, Ivoclar Vivadent, Italy) five from each disk were fabricated. From these molds, ten acrylic (DPI-RR Cold Cure, Dental products of India, Mumbai) specimens were made, five without graphene additives to serve as a control group and five with graphene additives (UGRAY, United Graphene, United Nanotech Innovations Pvt. Ltd, Bangalore) to serve as a test group (Fig.3).

An electronic balance (Shimadzu, India) was used to measure the graphene and polymer powders. 2% by weight of graphene (particle size of 25μm) was added in 100g of polymer: 33ml of monomer for the five test samples[9]. Similarly, the control samples were prepared using the same polymer: monomer ratio without the addition of graphene. The acrylic mixture was then poured into the putty molds and polymerized in a pressure pot (Vertex, curing pressure pot, Multicure) at 10MPa for 30 minutes. The polymerized disks were then finished and polished using tungsten carbide trimmers and silicone burs.

The samples thus obtained were tested using a thermal conductivity instrument (Unitherm Model 2022, Pittsburgh, USA)(Fig.4). This instrument uses the guarded hot plate principle to conduct heat[15]. Two plates, namely a hot plate and a cooling plate are in built in this instrument. The sample material was set between the two plates. One plate was heated and the other plate was cooled. The temperature of the plates were observed until they were constant (mean temperature of 55 was maintained). The steady-state temperatures, the thickness of the sample and the heat input to the hot plate were used to calculate thermal conductivity of the samples.

The results thus obtained were subjected to statistical analysis using the Mann Whitney U-test, a non-parametric test which considers the magnitude of the differences via ranks to test if two samples come from identical populations.

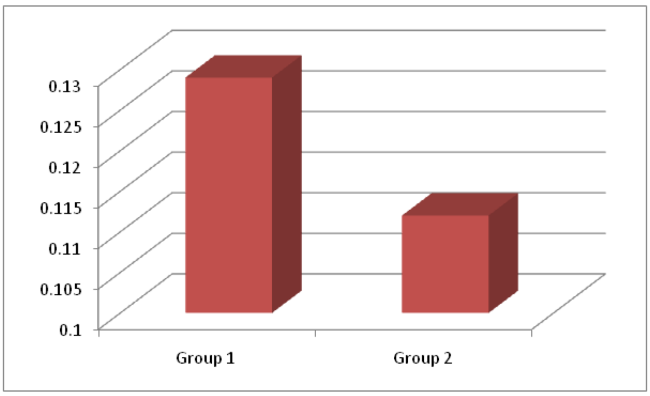
Table 1: Comparison of values between control and test groups

GROUP	VALUES (W/m/°C)	MEAN	STD. ERROR	STD. DEVIATION	p VALUE
Control	0.135				
	0.132				
	0.131				
	0.126				
	0.123	0.129	0.002	0.004	
Test	0.128				
	0.095				
	0.105				
	0.116				
	0.115	0.112	0.006	0.012	0.028

Results

The values obtained for the control group without the addition of graphene ranges from 0.123 W/m/°C to 0.135 W/m/°C with a mean of 0.129 and a standard deviation of 0.004(Table 1). The values for the test group ranges from 0.115 W/m/°C to

Chart 1



0.128 W/m/°C with a mean of 0.112 and standard deviation of 0.012 (Table 1). The p-value was found to be 0.028. This shows that the values have decreased consistently for the test group when compared to control group. The p-value is less than 0.05 which proves that the results are statistically significant.

Discussion

Polymethyl methacrylate has been dominating the dental industry for many years due to its near ideal mechanical and physical qualities. Numerous studies have been conducted in the past to enhance these properties by incorporating various fillers and fibers[16,18]. The enhancement of the thermal conductivity of PMMA has been experimented using materials like aluminium oxide, titanium oxide, zirconium oxide, silicon carbide filler powders, hydroxyapatite ceramic powders, silver nanoparticles and carbon particles[17,19].

In the present study, ten acrylic disks measuring 50 x 2±0.5mm were fabricated for thermal conductivity testing, five with graphene additives and five without graphene additives. These disks were polymerized and subjected to thermal conductivity testing. The values thus obtained were subjected to statistical investigation using Mann Whitney U non-parametric test. The p-value was found to be 0.028 ($p<0.05$). This shows that the study is statistically significant and the null hypothesis is rejected.

Results prove that thermal conductivity had reduced for the test group when compared to the control group. Thus, the addition of graphene additives has reduced the thermal conductivity of PMMA. The possible reasons for this finding could be the proportion of graphene in polymer/ monomer was inadequate. The quantity of graphene incorporated in the test samples lead to an acceptable discoloration which can be used for characterizing dentures. But the addition of more amount of graphene led to an unaesthetic dark discoloration of the material which would be unsuitable for fabricating the prosthesis[9]. Also, there could have been agglomeration of graphene particles since they were not subjected to a process called as ultra probe sonification[9]. The thermal conductivity instrument (Unitherm 2022, ASTM E 1530, CIPET/PTC/027. Anter Corporation, USA) can conduct heat equally only if the sample thickness is constant throughout with a variation of ± 0.5mm. There could have been possible variations in the thickness of the sample while finishing and polishing,this could have lead to varying values. The study was conducted involving a small sample size, further investigations can be done using a larger sample size. Also, heat cure denture base can be used.

Conclusion

Within the limitations of the present study, it can be concluded that,

1. Incorporation of graphene in PMMA, in the proportion of 2% by weight of graphene in 100g of polymer: 33ml of monomer ratio decreased its thermal conductivity.

2. The addition of graphene in PMMA did not significantly improve its thermal properties.

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